

THE INFLUENCE OF PROMOTER METALS ON THE CATALYTIC ACTIVITY OF A NANOSCALE SULFATED HEMATITE FOR THE LIQUEFACTION OF A SUBBITUMINOUS COAL

G. T. Hager, E. N. Givens, F. J. Derbyshire, The Center for Applied Energy Research, University of Kentucky, 3572 Iron Works Pike, Lexington, KY 40511-8433

Abstract

Nanoscale sulfated hematites ($\text{Fe}_2\text{O}_3 \cdot \text{SO}_4^{2-}$) have been shown to have high catalytic activity both for coal liquefaction and coprocessing of coal with a petroleum resid. The addition of small amounts of molybdenum as a promoter metal significantly enhances this catalytic activity. In this study, several metal promoted hematites have been prepared and characterized. The promoter metals studied include molybdenum, nickel, tungsten, and titanium. Various techniques were utilized to define both the bulk and surface chemistry of these materials, including XRD, SEM, TEM and XPS. The activity of these catalysts for the liquefaction of a subbituminous coal in tetralin will be reported.

Introduction

Several groups have investigated the use of sulfated hematites ($\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$) for use as both coal liquefaction and coprocessing catalysts with promising results.[1-8] It is important to note that this formula does not represent a stoichiometric relationship between the sulfate and the iron but rather the sulfate may be considered as SO_3 chemisorbed on the surface of Fe_2O_3 . Tanabe et al.[8] found that the sulfated hematite exhibited the highest activity, similar to that of a $\text{Co/Mo/Al}_2\text{O}_3$ catalyst, for the liquefaction of a bituminous coal. A study by Yokoyama et al [2] showed that the activity of the sulfated hematite was independent of the rank of the coal, yielding high conversions for both bituminous and subbituminous coals. In addition to a high conversion, these catalysts also showed a relatively high selectivity to oils.[1]

More recent work by Pradhan et al. [5-7] has shown the high activity of sulfated hematite for both direct coal liquefaction and coprocessing of coal with a Maya resid. The addition of up to 2 wt% molybdenum as a promoter metal further was found to further increase the activity of the catalyst. The highest conversions were achieved in the presence of added elemental sulfur with the catalyst. The high activities reported were achieved at very low catalyst loadings of <0.4 wt% Fe. This high activity is, in part, due to the small particle size and the associated high dispersion. XRD and TEM have both shown that the average particle diameter is 10-30 nm. The small size of these particles allows better contact with the coal. In addition, the presence of the sulfate group on the surface may inhibit the tendency of the particles to sinter during the liquefaction process. The increased acidity associated with the sulfate group also enhances the activity of the catalyst

for certain reactions.

Experimental

The technique used for production of the sulfated hematite involves the aqueous precipitation of an iron salt in the presence of a source of sulfate ion. There are several techniques used for this purpose. For this project, a urea precipitation of ammonium ferric sulfate was utilized. In this process 25 g of urea were mixed with 17.5 g of iron alum $[(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}]$ in 500 ml of distilled deionized water. The initial pH of the solution was ~3. The solution, stirred continuously during the process, was heated to ~95°C and kept at temperature for ~2 hrs. During this time the urea caused the gradual precipitation of the iron and a neutral pH was attained indicating the completion of the reaction.

The precipitate was removed from the solution by vacuum filtration and washed with distilled deionized water to remove unbound sulfate groups. The filter cake was dried to remove any residual moisture. The original technique called for calcination of the filter cake in air at 500°C for ~1 hr. Subsequent testing showed that for the small samples (~3g) generated in each batch calcining at ~475°C for ~10 minutes was sufficient.

Promoter metals may be added to the sulfated hematite by addition of metal containing salts to the solution. Molybdenum has been used, in the form of ammonium molybdate, to produce a sulfated hematite doped with molybdenum. Various concentrations of molybdenum have been added to determine the effect of loading on the activity. Several other metals, including tungsten, nickel, and cobalt were also added using this method. In addition, this procedure may be modified to add multiple promoter metals to the sulfated hematite. Several combination promoted sulfated hematite have been produced by this technique including nickel/molybdenum, cobalt/molybdenum, and tungsten/molybdenum.

XRD was utilized to identify the phase of the precipitated iron particles, both before and after calcination. As shown in Figure 1 the XRD spectra of the as-formed particles closely matches the reported spectra of goethite ($\alpha\text{-FeOOH}$). Also clearly shown in the spectra are the 44.7° and 65.0° peaks identified with $\alpha\text{-Fe}$. The relatively poor resolution in the XRD spectra is due to both the extremely small size and poor crystallinity of the particles. After calcining, the XRD spectra of the particles, shown in Figure 2, can clearly be identified as hematite ($\alpha\text{-Fe}_2\text{O}_3$) with the continued presence of the $\alpha\text{-Fe}$ peaks at 44.7° and 65°. The sharpness of the peaks in the calcined particles may be attributed to an increase in both the crystallinity and average particle size.

The chemisorbed sulfate group has been reported to have several effects on the catalytic properties of the particles.[5] One of the purposed function is the attainment and maintenance of high dispersion. The sulfate group may inhibit the particle agglomeration and sintering. The quantity of sulfur present was determined by elemental analysis to be 3-5 wt %. There was little effect of calcination on the sulfur content. The slight increase in concentration is easily accounted for by the mass loss which occurs during calcination.

The average crystallite diameter of the particles may be estimated from the XRD spectra. Utilizing this technique, the average particle sizes were shown to be in the 5 - 30 nm range with

most particles ranging from 15-20nm. SEM on the particles reveal that the particles exist as an agglomeration of very small particles below the resolution of the instrument. While this does not directly confirm the estimates made from the XRD spectra, neither does it refute them. TEM on the particles is in progress to validate the XRD derived estimates.

In order to determine the effect of residence time at temperature during calcination on the particle phase and size, a single batch of goethite was split into 4 samples. Each sample was calcined for between 10 and 60 minutes. The resulting catalysts were analyzed by XRD and the spectra were compared to determine phase and particle size. It was found that the transformation from goethite to hematite is complete within 10 minutes. However, the continued exposure to this temperature appeared to have little effect on the average diameter of the particles. There is some loss of surface area associated with the calcination process. Nitrogen BET measurements showed a decrease of the surface areas of ~18% during the calcination process.

The addition of molybdenum to the sulfated hematite as a promoter metal has been reported to improve the activity of the catalyst.[5] It was therefore decided to attempt to add varying amounts of molybdenum to the sulfated hematite to act as a promoter metal. The doping of the sulfated hematite with molybdenum was achieved by addition of ammonium molybdate to the iron alum/urea solution. Elemental analysis of both the product and the waste water indicate that all but a trace amount of the molybdenum is incorporated in the catalyst.

It has been reported that the role of the molybdenum in the catalyst structure is to deposit on the surface as MoO_3 [9]. Consequently, elemental analysis shows that the addition of molybdenum results in a decrease in the amount of sulfate present. Since the sulfate group is located primarily on the surface, this further confirms that the molybdenum acts to displace the sulfate group on the surface of the hematite. Further, the XRD spectra indicate that, even at concentrations up to 10 wt% molybdenum, only the hematite and $\alpha\text{-Fe}$ spectra were present indicating that the molybdenum is present either in an amorphous phase or on the surface.

The addition of molybdenum had a moderate effect on the particle diameter as determined from XRD spectra. As shown in Figure 3, the increase in the amount of molybdenum added led to a gradual decrease in the particle diameter. However, as the error bars indicate, this trend is somewhat dubious. The significant error is due to inaccuracies associated with the estimation of particle diameter from XRD spectra and also to the amount of noise present in the spectra. The molybdenum promoted sulfated hematites also appear as a loose agglomeration of particles whose size was below the resolution of the SEM.

Surface areas of the molybdenum promoted sulfated hematites were measured by the nitrogen BET method. The effect of increasing molybdenum concentration was to increase the surface area of the particles, as shown in Figure 4. As expected, since there is little to no porosity associated with these particles, the trend in surface area agrees with the trend seen in the particle diameter estimation. The replacement of the sulfur with molybdenum on the surface may lead to further inhibition of agglomeration due to the relative size of the atoms. This would agree well with both the surface area measurements and particle diameter estimations.

The catalysts were tested for use in the liquefaction of a subbituminous Black Thunder coal.

The experiments were carried out in horizontal 50 ml. microautoclave reactors. The conversions were determined by solubility using THF and pentane, into IOM, preasphaltenes + asphaltenes, and oils. The gas yields were determined directly by GC. Two sets of reactions were carried out to determine the effect of severity on catalytic activity. The low severity experiments were conducted at 385°C for 15 minutes while the high severity conditions were carried out at 415°C for 60 minutes. All runs were done in duplicate to assure reproducibility. As shown in Table 1, preliminary results indicate that, for a catalyst loading of 0.7 wt % Fe at high severity conditions, while all catalysts displayed similar total conversions (~89%), the use of molybdenum resulted in the greatest increase in conversion to oils (~39%). The nickel doped sulfated hematite showed a slightly higher total conversion (~90 %) but a lower selectivity to oils (~33 %). Tungsten and cobalt yielded similar total conversions (~89 %) and oil yields (~37 %). These results show that these catalysts compare favorably with a commercially available 30 Å superfine iron oxide, while their lower cost and ease of production make them economically more viable for scale up.

References

- 1) Hattori, H; Yamaguchi, T; Tanabe, K.; Yokoyama, S; Umematsu, J; Sanada, Y.; *Fuel Proc Tech*, **8**, 117-22, 1984
- 2) Yokoyama, S; Yamamoto, M; Yoshida, R; Mackawa, Y; Kotanigawa, T; *Fuel*, **70**, 163-8, 1991
- 3) Kotanigawa, T; Yokoyama, S; Yamamoto, M; Mackawa, Y; *Fuel*, **68**, 618-21, 1989
- 4) Huffman, G P; Ganguly, B; Taghiei, M; Huggins, F E; Shah, N; *Preprint ACS- Div of Fuel Chem*, **36**(2), 561-9, 1991
- 5) Pradhan, V R; Herrick, D E; Tierney, J W; Wender, I; *Energy & Fuels*, **5**, 712-20, 1991
- 6) Pradhan, V R; Tierney, J W; Wender, I; Huffman, G P; *Energy & Fuels*, **5**, 497-507, 1991
- 7) Pradhan, V R; Tierney, J W; Wender, I; *Preprint ACS- Div of Fuel Chem*, **35**(3), 793-800, 1990
- 8) Tanabe, K; Hattori, H; Yamaguchi, T; Iizuka, T; Matsushashi, H; Kimura, A; Nagase, Y; *Fuel Proc tech*, **14**, 247-60, 1986
- 9) Pradhan, V R; Hu, J; Tierney, J W; Wender, I; *Preprint ACS- Div of Fuel Chem*, **38**(1), 8-13, 1993

Table 1. Effect of Catalyst on Liquefaction Yields

	% Total Conversion	% PA&A	% Oils	% Gas
SFIO	87.0	45.2	34.6	7.2
1%Mo/Fe ₂ O ₃ /SO ₄ ²⁻	88.5	43.1	38.9	6.8
5%Co/Fe ₂ O ₃ /SO ₄ ²⁻	88.8	45.6	36.6	6.6
5%W/Fe ₂ O ₃ /SO ₄ ²⁻	88.9	45.3	36.8	6.8
5%Ni/Fe ₂ O ₃ /SO ₄ ²⁻	90.4	49.8	33.4	7.1

Figure 1. XRD Spectra of As-formed Particles with Goethite and α -Fe

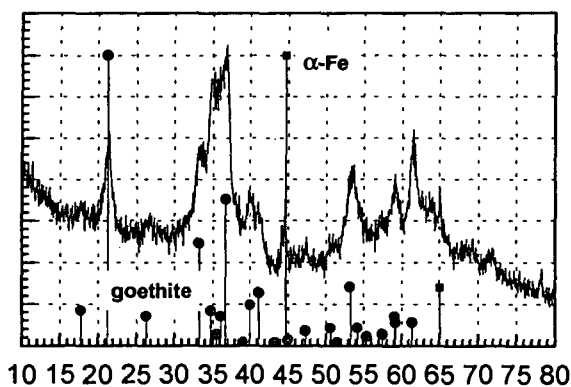


Figure 2. XRD Spectra of Calcined Particles with Hematite and α -Fe

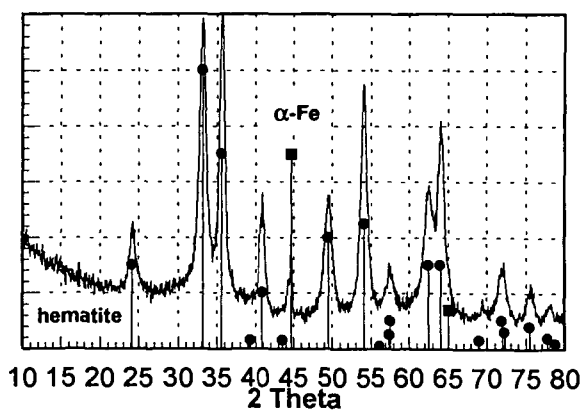


Figure 3. Effect of Molybdenum Concentration on Particle Diameter Estimated from XRD

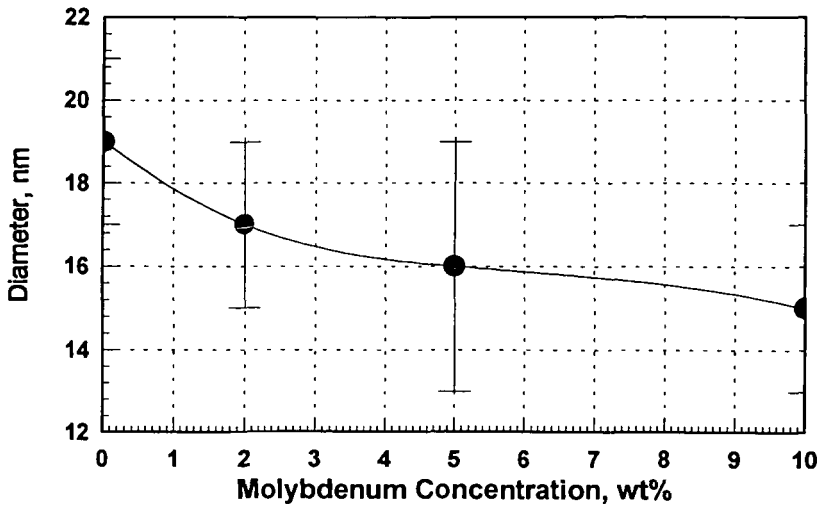


Figure 4. Effect of Molybdenum Concentration on Surface Area

